

Reply to anonymous referee #2

We thank you very much for providing valuable comments on our manuscript. The two issues you presented in the general comments are indeed important and are well worth discussing. We found that these general comments are all involved in your specific comments, therefore, we will address these issues and concerns in the responses to the specific comments one by one in below.

1. Lines 3 and 4 of the page 9473, the author indicated that there is oxidation of organic matter in rivers, and in the line 7 of the same page the author also indicated “through interim processes such as microbial utilization”. Indeed, they are all very important biogeochemical processes in the river water, and mainly bacteria and fungi involved in the decomposition of aquatic organic matter. However, in the later analysis (such as in the line 14 of page 9478, and the part of 4.1.2 of the manuscript), the author does not seem to consider the decomposition of bacteria and fungi in the water.

Response: In-river photosynthesis and decomposition (respiration) of organic matter is two simultaneous processes. The former decreases the $\delta^{13}\text{C}$ value of the DIC in the river, while the later increases the $\delta^{13}\text{C}$ value. The relative efficiency of these two simultaneous actions depends on the hydrology and residence time of water in river. Our isotopic analysis of DIC is in fact to examine the integrate status or, in other words, the final efficiency of the two processes. However, this contribution of decomposition of terrestrial organic to DIC is insignificant (<5%) according to a previous study on a river developed in carbonate-dominated areas (Aucour et al., 1999). In our revised version of the manuscript, we will clarify this issue with additional references.

2. In the lines from 12 to 14 of page 9473, narrative content and referred literatures is not matched. Those references do not focus on the Xijiang River.

Response: This sentence has been modified as below:

...riverine organic carbon is mainly composed of young terrestrial carbon originating from modern biosphere.... (“in the Xijiang river” is deleted from the sentence).

3. In the line 16 of page 9475, in the presence of pollution, the particles in the clay will absorb the NH_4^+ ion, if you don't eliminate out this part of inorganic N, which will result in the POM C/N ration decreased.

Response: Before lab analysis of POC and PN, the samples were treated with HCl, which could remove large part of the the NH_4^+ absorbed by clays. Previous studies showed that the inorganic N fraction is small (Meybeck, M., 1982. [Carbon, nitrogen, and phosphorus transport by world rivers. American Journal of Science 282: 401-450](#)), and a number of papers also use the PN instead of PON, for example, Trefry et al., 1994 (Trefry, J.H., Neisen, Terry, Trocine, R.P., Eadie, B.J., 1994. [Transport of Particulate Organic Carbon by the Mississippi River and Fate in the Gulf of Mexico. Estuaries 17: 839-849](#)), and other studies ([see the listed references below](#)). Accordingly, we think that the seasonal and spatial variation patterns of POC/PN ratio obtained in our study could largely reflect the

difference of particulate organic matter sources, though some inorganic N may still exist in the PN.

Martinotti, W., Camusso, M., Guzzi, and L., 1997. C, N and their stable isotopes in suspended and sedimented matter from the Po estuary (Italy). *Water, Air and Soil Pollution* 99: 325-332),

Pettine, M., Patrolocco, L., Camusso, M., and Crescenzo, S., 1998. Transport of Carbon and Nitrogen to the Northern Adriatic Sea by the Po River. *Estuarine, Coastal and Shelf Science* 46, 127-142.

Zhang, J., Wu, Y., Jennerjahn, T.C., Ittekkot, V., He, Q., 2007. Distribution of organic matter in the Changjiang (Yangtze River) Estuary and their stable carbon and nitrogen isotopic ratios- Implications for source discrimination and sedimentary dynamics. *Marine Chemistry* 106: 111-126.

Goñi, M.A., Teixeira, M.J., Perkey, D.W., 2003. Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). *Estuarine, Coastal and Shelf Science* 57: 1023-1048.

4. In the lines from 7 to 9 of page 9477: the author indicated that “DIC shows a decline trend from upstream to downstream, consistent with the fact that carbonate is mainly exposed in the upper reaches, indicating the dominate impact of carbonate weathering on the riverine DIC concentration of the region” which statements are conflicted with the increasing biomass of algae downstream.

Response: We don't agree. The downstream decline trend of DIC does not conflict with the increasing biomass of algae downstream, In contrast, they are well consistent, because the downstream increasing aquatic biomass (mainly algae) must cause downstream increasing consumption of DIC and thus downstream decline of DIC concentration.

5. In lines 1 to 3 of page 9480, the author indicated that “producing equal contributions of both carbonate and soil CO₂ to the DIC, resulting in a mid $\delta^{13}\text{C}$ value of the DIC between the two sources”, and in the lines 6 and 7 of the same page, “DIC from silicate rock weathering will have the same $\delta^{13}\text{C}$ value as soil CO₂”. The reviewer suggested that there is an isotopic fractionation from soil CO₂ to aquatic HCO₃⁻, which is about ~9‰ (Clark and Fritz, 1997). The author should have not ignored of this. The lines from 14 to 23 of the same page, isotopic fractionation from soil CO₂ to aquatic HCO₃⁻ was not considered completely, i.e., the ionization process from aquatic CO₂ into HCO₃⁻ (the fractionation factor is ~9‰).

Response: The isotopic fractionation from soil CO₂ to aquatic HCO₃⁻ is indeed an important issue and should be addressed sufficiently in the manuscript. It should be pointed out that this process (soil CO₂ to aquatic HCO₃⁻) how to impact the resultant carbon isotopic composition during carbonate weathering is also depended on the degree to which the water–mineral system is ‘open’ to the CO₂ gas reservoir during weathering (Clark and Fritz, 1997; Aucour et al., 2001). In a completely open system, the carbon isotopic composition involved in the chemical weathering is still dominated by soil CO₂, because of the continuous exchange between CO₂ and the solution. The Xijiang basin as

a carbonate-dominated region is an open system during rock chemical weathering (Aucour et al., 1999; Kanduč et al., 2007; Li et al., 2008), thus the $\delta^{13}\text{C}$ value of the produced DIC during carbonate weathering should be determined by the soil CO_2 .

In response to your concern we have modified and added more explanation for the relevant part of the section 4.1.1 in the revised manuscript as follows (marked sentences with yellow color are added sentences):

From line 21 of pg 9479:

CO_2 involved in the reactions is mainly from soil zone where $p\text{CO}_2$ values are 2-3 orders of magnitude higher than the atmosphere (Berner and Berner, 1996). Dissolution of soil CO_2 into soil water produces a $\sim 9\text{‰}$ fractionation of ^{13}C that is dependent on pH and temperature (Clark and Fritz, 1999). However, the $\delta^{13}\text{C}$ of DIC produced by carbonate rock weathering with CO_2 should depend on, besides the isotopic composition of biogenic CO_2 , whether it is an 'open' or 'close' system during weathering (Mook and Tan, 1991; Clark and Fritz, 1997). Under open system condition, $\delta^{13}\text{C}$ of DIC will be dominated by soil CO_2 because of continuous exchange between soil CO_2 and the solution. Like other carbonate-dominated regions (Aucour et al., 1999; Kanduč et al., 2007; Li et al., 2008), the Xijiang basin is an open system, where nonequilibrium dissolution of carbonates should produce an intermediate $\delta^{13}\text{C}$ value of DIC between the soil CO_2 and the carbonate mineral (Mook and Tan, 1991; Kanduč et al., 2007). Carbonate dissolution with sulfuric acid (Eq.2) is also an important source of DIC for the Xijiang river system (Xu et al., 2007; Li et al., 2008), in which all the DIC is derived from carbonate, thus has identical $\delta^{13}\text{C}$ values to the carbonate minerals. DIC from silicate rock weathering (Eq.3) will have the same $\delta^{13}\text{C}$ value as soil CO_2 .

$\delta^{13}\text{C}$ value of DIC from carbonate and silicate weathering can be calculated using

the following end-member mixing model.

$$\delta^{13}\text{C}_{\text{DIC}} = f_{\text{cc}} * \delta_{\text{cc}} + f_{\text{cs}} * \delta_{\text{cs}} + f_{\text{sc}} * \delta_{\text{sc}} \quad (4)$$

$$f_{\text{cc}} + f_{\text{cs}} + f_{\text{sc}} = 1 \quad (5)$$

Where f represents fraction, subscripts cc , cs and sc denote the chemical weathering of carbonate with CO_2 , carbonate with H_2SO_4 , and silicate with CO_2 respectively.

In general, soil CO_2 converted from soil POC by microbial activities will nearly have no isotope fractionation (Cerling et al., 1995). For the Xijiang basin, the fractionation by this process has been accurately assessed to be $-0.5\sim-1.5\text{‰}$ (Pan and Guo, 1999). Using the soil POC $\delta^{13}\text{C}$ signatures (-22.6‰ , Table 3) and a mean fractionation value (-1‰), the $\delta^{13}\text{C}$ of soil CO_2 in the Xijiang basin can be determined as -23.6‰ , consistent with the measured $\delta^{13}\text{C}$ ($-24.0\sim-20.9\text{‰}$) of soil CO_2 in the Xijiang basin (Pan et al., 2002). Given the $\delta^{13}\text{C}$ of carbonate rocks in this region to be 0.4‰ (Li, 1994), the $\delta^{13}\text{C}$ values of DIC from chemical weathering of carbonate with CO_2 , carbonate with H_2SO_4 , and silicate with CO_2 (δ_{cc} , δ_{cs} and δ_{sc}) are estimated to be -11.3‰ , 0.4‰ and -23.6‰ , respectively.

6. In the lines 13 and 14 of page 9483, the author indicated that “This implies an all-year excess of production over respiration in the Xijiang river system, but close to zero during the flood event”, which is conflicted with the large pCO_2 in the river.

Response: Yes, I basically agree with you. To avoid confusion, we have modified this sentence as “This implies that in-river aquatic primary production has an all-year dominant influence over respiration on carbon-isotope compositions of the riverine POC and DIC in the Xijiang river system, with exception of a nearly null effect during the extreme flood

event.”

7. In the lines 21 and 22 of page 9483, the author indicated that “bacteria can grow by directly using bicarbonate”. The bacteria are the decomposers, and can not directly use HCO_3^- to produce organic matter.

Response: Yes, I agree. In the revised version, we have modified this sentence as “aquatic plant such as algae can grow by directly using bicarbonate”.